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TITLE OF THE INVENTION (*280 characters max*)

Method and System for Photo-Assisted Atomic Layer Deposition and Removal

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STATE	CA	ZIP CODE	94111	COUNTRY	US

ENCLOSED APPLICATION PARTS (*check all that apply*)

X	Specification	*Number of Pages*	10 total		Small Entity Statement
X	Drawings	*Number of Sheets*	15	X	Other (*specify*): 1 page(s) of Claims

METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT (*check one*)

	A check or money order is enclosed to cover the Provisional filing fees		PROVISIONAL FILING FEE AMOUNT ($)	$160.00
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.

[X] No.

[ ] Yes, the name of the U S. Government Agency and the Government contract number are: ____________

Respectfully submitted,

SIGNATURE: *[signature]* Date: June 23, 2002

TYPED or PRINTED NAME: Maria S. Swiatek REGISTRATION NO. (*if appropriate*): 37,244

[ ] Additional inventors are being named on separately numbered sheets attached hereto.

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1043634

METHOD AND SYSTEM FOR PHOTO-ASSISTED ATOMIC LAYER DEPOSITION AND REMOVAL

FIELD OF THE INVENTION

The present invention relates generally to the field of semiconductors. More specifically, the present invention relates to photo-assisted atomic layer deposition and removal of films on semiconductor devices and wafers.

BACKGROUND OF THE INVENTION

Semiconductor devices of future generation require thinner dielectric films for MOS transistor gates, and capacitor dielectrics. As oxides are scaled down, the tunneling leakage current becomes significant and limits the useful range for gate oxides to about 1.8 nm or more.

High dielectric constant metal oxides such as HfO_2 (k=20), ZrO_2 (k=20) and Hf and Zr silicates are considered alternative materials to silicon oxide (k=3.9) to provide gate dielectrics with high capacitance without compromising the leakage current. However, prior art deposition techniques such as chemical vapor deposition (CVD) are increasingly unable to meet the requirements of advanced thin films. While CVD processes can be tailored to provide conformal films with improved step coverage, CVD processes often require high processing temperatures, result in incorporation of high impurity concentrations, and have poor precursor or reactant utilization efficiency. For instance, one of the obstacles of making high k gate dielectrics is the formation of an interfacial silicon oxide layer during CVD processes. Another obstacle is the limitation of prior art CVD processes in depositing ultra thin films for high k gate dielectrics on a silicon substrate.

Atomic layer deposition (ALD) is an alternative to traditional CVD processes to deposit very thin films. ALD has several advantages over traditional CVD. ALD can be performed at comparatively lower temperatures which is compatible with the industry's trend toward lower temperatures, has high precursor utilization efficiency, and can produce conformal thin film layers. More advantageously, ALD can control film thickness on an atomic scale, and can be used to "nano-engineer" complex thin films. Accordingly, further developments in ALD are

highly desirable.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a method and system of forming films on semiconductor devices and wafers by photo-assisted atomic layer deposition and removal.

It is an another object of the present invention to provide a method of depositing a metal containing film on a substrate without forming an interfacial oxide layer between the metal containing film and the substrate.

It is another aspect of the present invention to provide a method of removing a material (dielectric or metal) at low temperatures.

In one aspect of the invention, there is provided a method of photo atomic layer deposition (PALD) of a film on a substrate. According to the PALD method of the invention, a substrate having an film deposited on the surface of the substrate is first pre-treated to form a stable, activated surface. The substrate having a stable, activated surface is then placed into a reactor maintained at a low temperature and high vacuum. A first gaseous precursor is introduced into the reactor about the substrate. The gas and substrate are exposed to a first pulse of electromagnetic irradiation and radical species are formed. The radicals react with the activated surface to terminate the surface with the radical species. Then a second precursor is introduced into the reactor and a second pulse of electromagnetic irradiation is initiated to form different radicals from the second precursor. The different radicals react with the terminated surface to form an atomic layer of material on the surface of the substrate.

BRIEF DESCRIPTION OF THE FIGURES

The foregoing and other objects of the invention will be more clearly understood from the following description when read in conjunction with the accompanying drawings in which:

Figure 1 is a schematic view illustrating an interfacial silicon oxide layer formed between a metal containing layer and silicon substrate during a prior art deposition process.

Figure 2 is a schematic view illustrating a reactor for carrying out the photo atomic layer deposition method according to one embodiment of the present invention.

Figure 3 is a schematic view illustrating an alternative reactor for carrying out the photo atomic layer deposition method according to another embodiment of the present invention.

Figures 4A to 4J are schematic diagrams illustrating the steps of atomic layer exchange for formation of a 5EOT gate dielectric according to another embodiment of the present invention.

Figures 5 and 6 are tables showing examples of liquid Hf precursors and liquid Zr precursors, respectively.

Figure 7 is a chart describing example applications for high κ gate dielectrics.

DETAILED DESCRIPTION OF THE INVENTION

In general, the present invention provides a method and system of forming films on semiconductor devices and wafers by photo-assisted atomic layer deposition and removal. More specifically, in one embodiment of the present invention, a method of photo atomic layer deposition (PALD) of a film on a substrate is provided. The PALD method of the invention may be carried out as follows: a substrate having an film deposited on the surface of the substrate is first pre-treated to form a stable, activated surface. The substrate having a stable, activated surface is then placed into a reactor or chamber maintained at a low temperature and high vacuum. A first gaseous precursor is introduced into the reactor about the substrate. The gas and substrate are exposed to a first pulse of electromagnetic irradiation and radical species are formed. The radicals react with the activated surface to terminate the surface with the radical species. Then a second precursor is introduced into the reactor and a second pulse of electromagnetic irradiation is initiated to form different radicals from the second precursor. The different radicals react with the terminated surface to form an atomic layer of material on the surface of the substrate.

As illustrated in FIG. 1, an undesired interfacial silicon oxide layer is commonly formed between a metal oxide and silicon substrate during prior art depositions. One way to provide a clean interface between the metal oxide and silicon substrate is to perform a deposition process at a low temperature ranging from 120-150 °C. However, chemical molecules are usually not

activated at such low deposition temperatures. The present invention provides a solution to this problem by carrying out a photo-assisted atomic layer deposition at a low temperature and high vacuum, thus providing a clean interface between the metal oxide film and substrate.

The present invention is further described with reference to FIGs. 2 and 3 which schematically illustrates a high vacuum, low temperature reactor that can be used to perform photo-assisted atomic layer deposition of the invention. While a specific reactor is shown for illustrative purpose, other reactor designs may be used and the present method is not limited to any one reactor or chamber design. The present PALD method can be performed in any suitable reactors such as a single wafer reactor and multiple wafer reactor. The pressure within the reactor is maintained under vacuum, and preferably is below 1 torr.

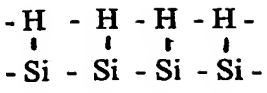
In an illustrative example of the method and system of the present invention, a substrate having an oxide film deposited on the surface of the substrate is first pre-treated to form a hydrogen-terminated surface. The substrate having a hydrogen-terminated surface is then placed in a reactor maintained at a low temperature and high vacuum. An oxygen containing gas is introduced into the reactor above the substrate and a first pulse of electromagnetic irradiation is imposed to the oxygen containing gas to form oxygen radicals. The oxygen radicals react with the hydrogens at the silicon dangling bonds at the hydrogen-terminated surface. An oxygen terminated surface is formed after atomic layer exchange between the hydrogen and oxygen. Then a metal precursor is introduced into the reactor and a second pulse of electromagnetic irradiation is imposed to break up the metal precursor molecules and form metal radicals. The metal radicals react with the oxygen terminated surface to form an atomic layer of metal oxide on the surface of the substrate.

In the illustrative example where the substrate has an oxide deposited on the surface of the substrate, the following structure is present:

$$\begin{array}{cccc} -\mathrm{O} & -\mathrm{O} & -\mathrm{O} & -\mathrm{O}- \\ | & | & | & | \\ -\mathrm{Si} & -\mathrm{Si} & -\mathrm{Si} & -\mathrm{Si}- \end{array} \qquad (1)$$

For pretreatment, the substrate having oxides deposited on the surface is dipped in a weak hydrogen fluoride (HF) solution to create a hydrogen-terminated surface as shown in the

following structure:



(2)

The substrate having the hydrogen-terminated surface is then placed in a reactor which is maintained at a low temperature and high vacuum. An oxygen containing gas is introduced into the reactor above the substrate. Examples of the oxygen containing gas include (but not limited to) O_2, NO, N_2O, H_2O, H_2O_2, and the like. The oxygen containing gas can be introduced into the reactor in various ways and is delivered about the substrate. For example, the oxygen containing gas can be introduced into the reactor from the top or the sidewall of the reactor. The hydrogen-terminated surface is exposed to the oxygen containing gas. However, the oxygen containing gas does not react with the hydrogen at the substrate surface due to the low temperature and pressure maintained in the reactor.

To activate the reaction, a first pulse of electromagnetic irradiation is initiated which activates the oxygen containing gas above the surface of the substrate to form oxygen radicals. Any form of electromagnetic irradiation can be used, and preferably the electromagnetic irradiation is pulsed. For example, electromagnetic irradiation can be photo UV, magnetic field, or microwave energy. The selection of electromagnetic irradiation depends on the application and the type of film to be deposited. While microwave energy may create an electrical field across the substrate, photo UV does not create an electrical field and thus is preferable for applications where electrical fields should be avoided. The electromagnetic irradiation can emanate from the top of the reactor, or may be focused to a particular localized region or area on the substrate. Alternatively, in a multiple wafer reactor, a side wall scanning laser can be used to sequentially expose multiple substrates to the electromagnetic radiation pulses. A side wall scanning laser is advantageous in a multiple wafer reactor. Alternately, a focused source of electromagnetic radiation can be used to activate the PALD process on selected areas of the substrate (i.e. direct write).

In the exemplary embodiment, the oxygen radicals formed react with hydrogen at the

irradiation is imposed as a pulse. For example, the electromagnetic irradiation can be photo UV, magnetic field, and microwave. The selection of electromagnetic irradiation depends on the application and the type of film to be removed. While microwave energy may create electrical field across the substrate, photo UV does not create electrical field and thus is good for applications where electrical field should be avoided. The electromagnetic irradiation can be imposed from the top of the reactor to a particular local area above the substrate. Alternatively, in a multiple wafer reactor, a side wall scanning laser can be used to impose electromagnetic irradiation to the multiple substrates sequentially. A side wall scanning laser is advantageous in a multiple wafer reactor. Alternately, a focused source of electromagnetic radiation can be used to activate the PALR process on selected areas of the substrate (i.e. "direct write" removal). The radical species react with the surface to form volatile compounds which are removed from the reactor. The process can be repeated to remove atomic layers of films at low temperatures.

Another exemplary embodiment of the present invention is illustrated in FIGs. 4A to 4J which show sequential steps in detail. In this example atomic layer exchange is carried out with photo-assist to form a gate dielectric having an equivalent oxide thickness (EOT) of 5. Atomic layer exchange is carried out to modify the chemistry of the film surface. As show in FIG. 4A, a silicon wafer having a hydrogen passivated surface is provided. Next, an oxygen source is conveyed to the chamber about the wafer. The oxygen source is activated by electromagnetic radiation as shown in FIG. 5C. The activated oxygen source undergoes a surface reaction with the wafer and exchanges hydrogen atoms with oxygen atoms to form one, or one half, atomic layer of oxide on the wafer as shown in FIG. 5D. They reactor is then purged.

Next, a precursor which will produce the desired gate dielectric material is conveyed to the chamber. In this example, a Hf containing source is the precursor. The Hf precursor is activated by a pulse of electromagnetic radiation, such as a UV photo pulse, under low temperature as shown in FIGs. 4F and 4G. Atomic layer deposition occurs on the surface of the wafer as shown in FIG 4H, and then the reactor is purged, preferably with the assistance of argon gas.

To form the dielectric, in this example Hafnium oxide, an oxygen source is again conveyed to the reactor as shown in FIG. 4I. The oxygen source is activated by a photo pulse,

and atomic layer deposition occurs to form a HfO_2 layer on the surface of the wafer. The oxygen source is purged (FIG. 4J) from the reactor and the process may be repeated to form additional atomic layers as desired.

As described above, atomic layer exchange takes place between free radicals or molecules in the gas phase and the wafer surface. Diffusion of these gaseous precursors through the wafer surface may be controlled by a number of parameters, including temperature, pulse time, chamber pressure, molecule size and reactivity - to avoid multilayer atomic exchange.

The photo-assisted atomic layer deposition and removal method of the present invention has broad applications. For example, the present invention can be used to etch metals and dielectrics, generate photolithographic masks, and improve resolution of liquid crystal displays, among other applications. Additionally, atomic layer removal of the present invention may be used for reducing final film thicknesses and/or removing undesired surface roughness prior to forming gate electrodes. High quality high-κ dielectric films can be deposited with selected ALD precursors at low deposition temperature with photo activation. Examples of suitable liquid Hf and liquid Zr precursors are shown in FIGS. 5 and 6, respectively. The silicon - high κ dielectric interface may be controlled by atomic layer exchange of the present invention along with low temperature ALD high κ dielectric processes. Additional applications for high - κ gate dielectric applications are shown in FIG. 7.

While the present invention is disclosed by reference to the preferred embodiments and examples detailed above, it is to be understood that these examples are intended in an illustrative rather than limiting sense, as it is contemplated that modifications and combinations will readily occur to those skilled in the art, which modifications and combinations will be within the scope of the invention and the scope of the appended claims.

CLAIMS

What is claimed:

1. A method of depositing a film on a substrate, comprising:

providing a substrate having an film deposited on the surface of the substrate;

pre-treating the substrate to form a stable, activated surface on the substrate;

introducing a first gas into the reactor at a low temperature and pressure;

providing a first pulse of electromagnetic irradiation about the substrate to form radicals species from said first gas;

reacting the radicals with the stable, activated surface to form an radical terminated surface on the substrate;

introducing a second gas into the reactor at a low temperature and pressure; and

providing a second pulse of electromagnetic irradiation about the substrate to form different radicals species from said second gas; and

reacting the different radicals with the radical terminated surface to form a layer of film on the substrate.

2. A method of removing a film on a substrate, comprising:

providing a substrate having an film deposited on the surface of the substrate;

pretreating the substrate to form a stable, activated surface on the substrate;

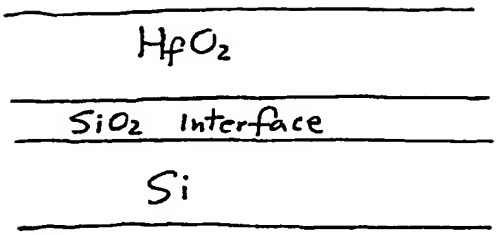
introducing a gas into the reactor at a low temperature and pressure;

providing a first pulse of electromagnetic irradiation above said substrate to form radical species from said gas; and

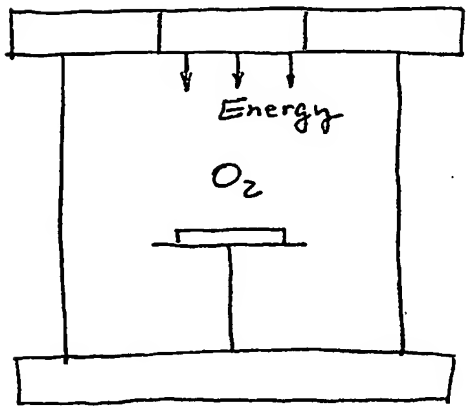
reacting the radicals with the stable, activated surface to form a volatile compound which is removed from the reactor.

ABSTRACT

A method and system for photo-assisted atomic layer deposition and removal of a dielectric film are provided. A substrate with an activated surface is placed into a reactor at low temperature and high vacuum. A gas is introduced into the reactor. An electromagnetic pulse is imposed into the reactor to form radical species of the gas. The radical species react with the activated surface. A second gas is introduced and a second electromagnetic pulse is imposed. The radicals of the second gas react with the surface to deposit a film. Alternately, the gaseous species can be chosen to produce radicals that result in the removal of material from the surface.



FIG—1



FIG—2

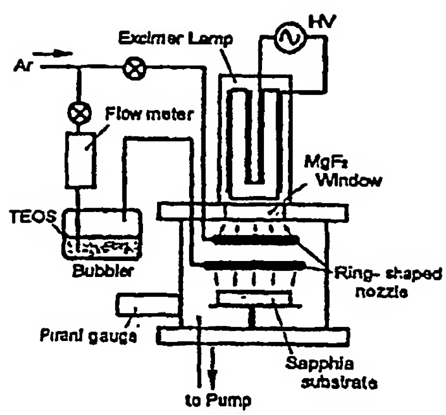
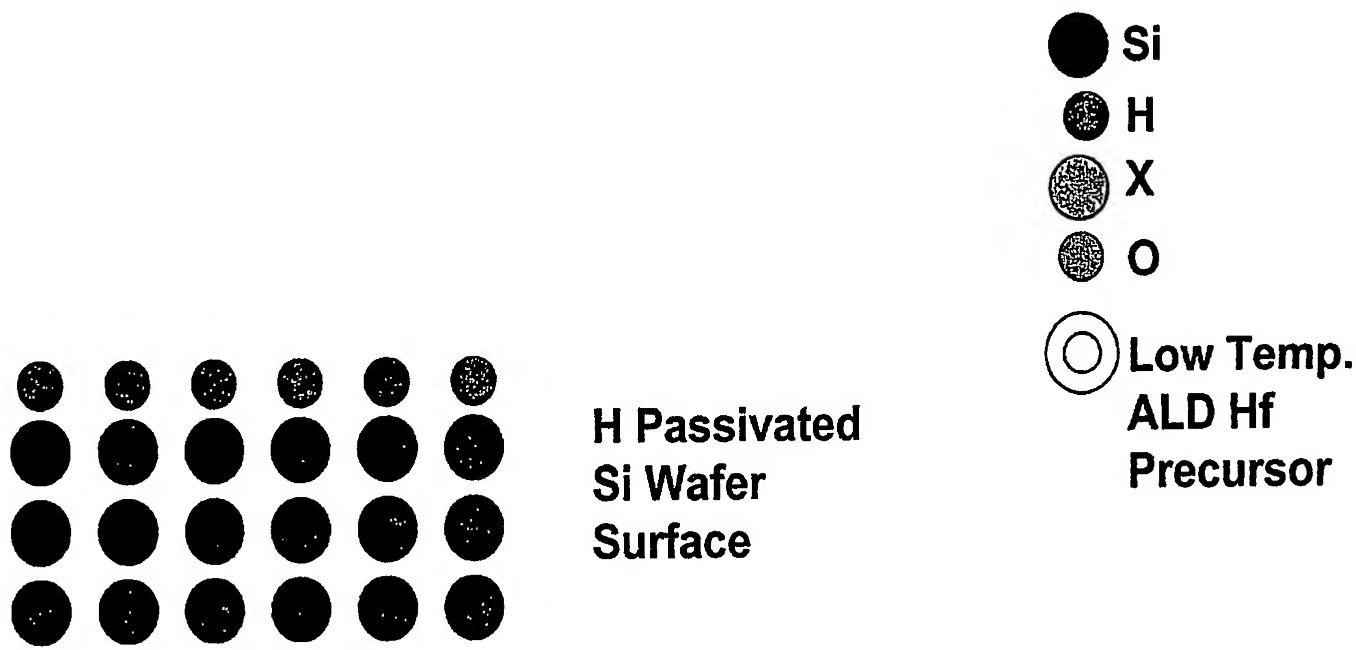

HV
Excimer Lamp
Ar
Flow meter
MgF₂
Window
TEOS
Bubbler
Ring- shaped
nozzle
Pirani gauge
Sapphia
substrate
to Pump

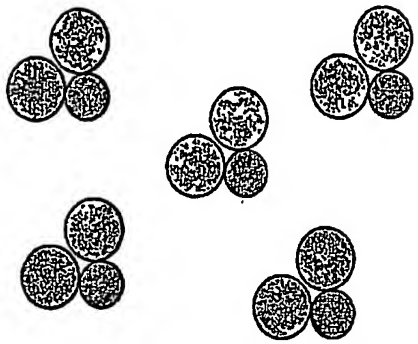
FIG _ 3

Atomic Layer Exchange For 5 EOT Gate Dielectric

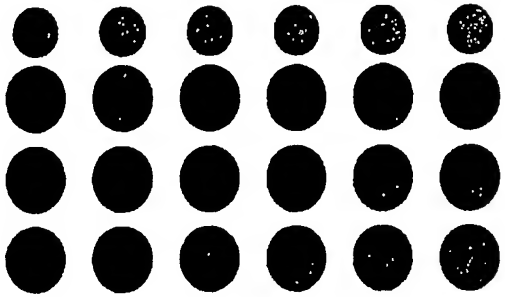


FIG—4A

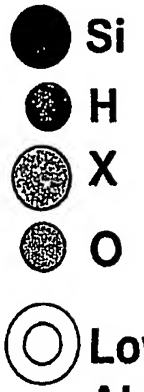
Atomic Layer Exchange For 5 EOT Gate Dielectric



Pulse Oxygen Source



H Passivated Si Wafer Surface



Low Temp. ALD Hf Precursor

FIG- 4B

Atomic Layer Exchange For 5 EOT Gate Dielectric

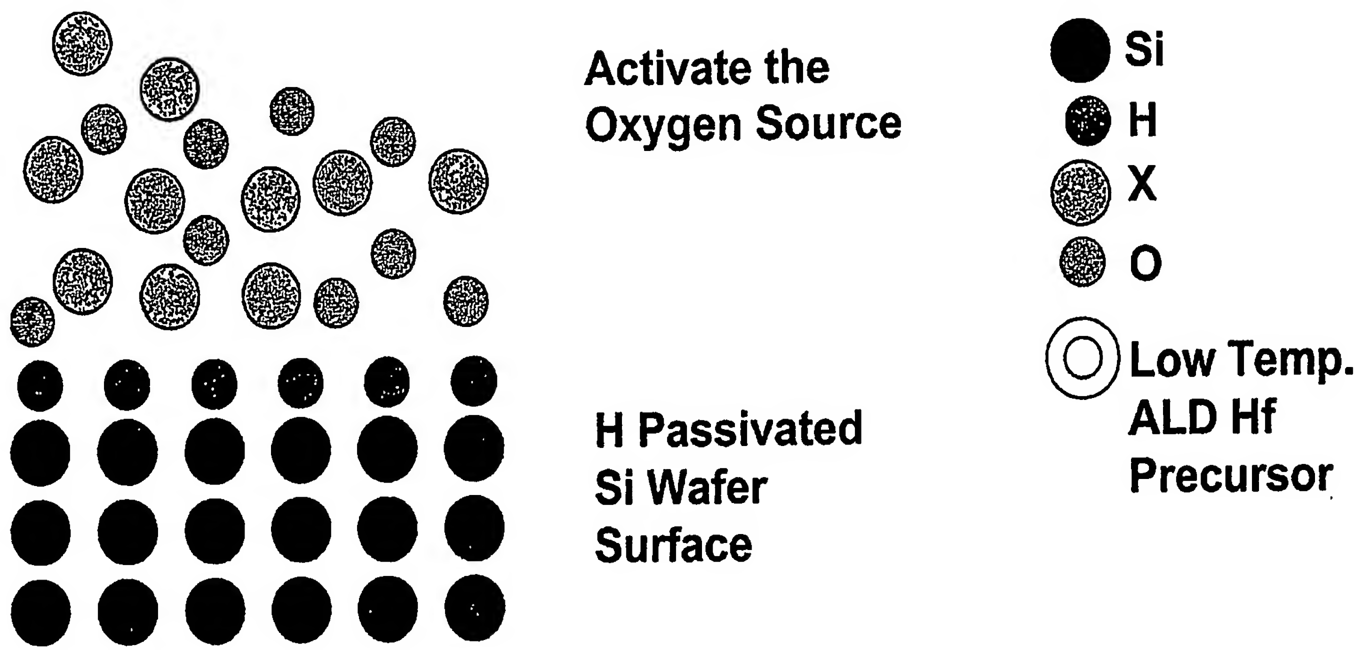
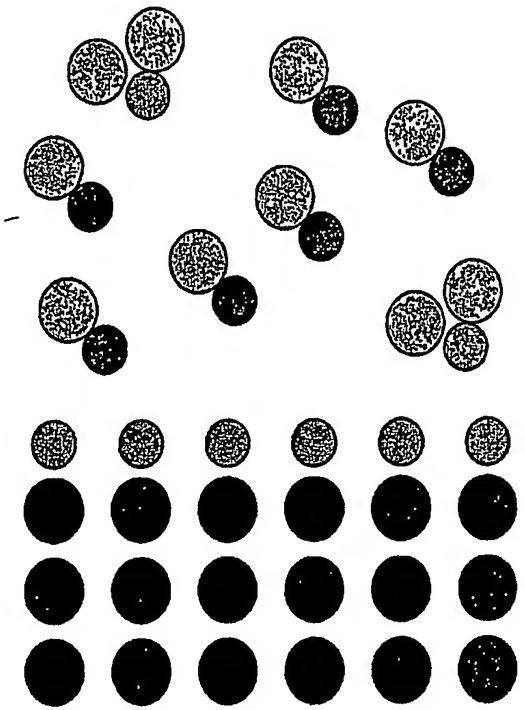


FIG-4C

Atomic Layer Exchange For 5 EOT Gate Dielectric



Exchange of H atoms with O atoms to form 1 or 1/2 Atomic Oxide

H Passivated Si Wafer Surface

Si
H
X
O

Low Temp. ALD Hf Precursor

FIG-4D

Atomic Layer Exchange For 5 EOT Gate Dielectric

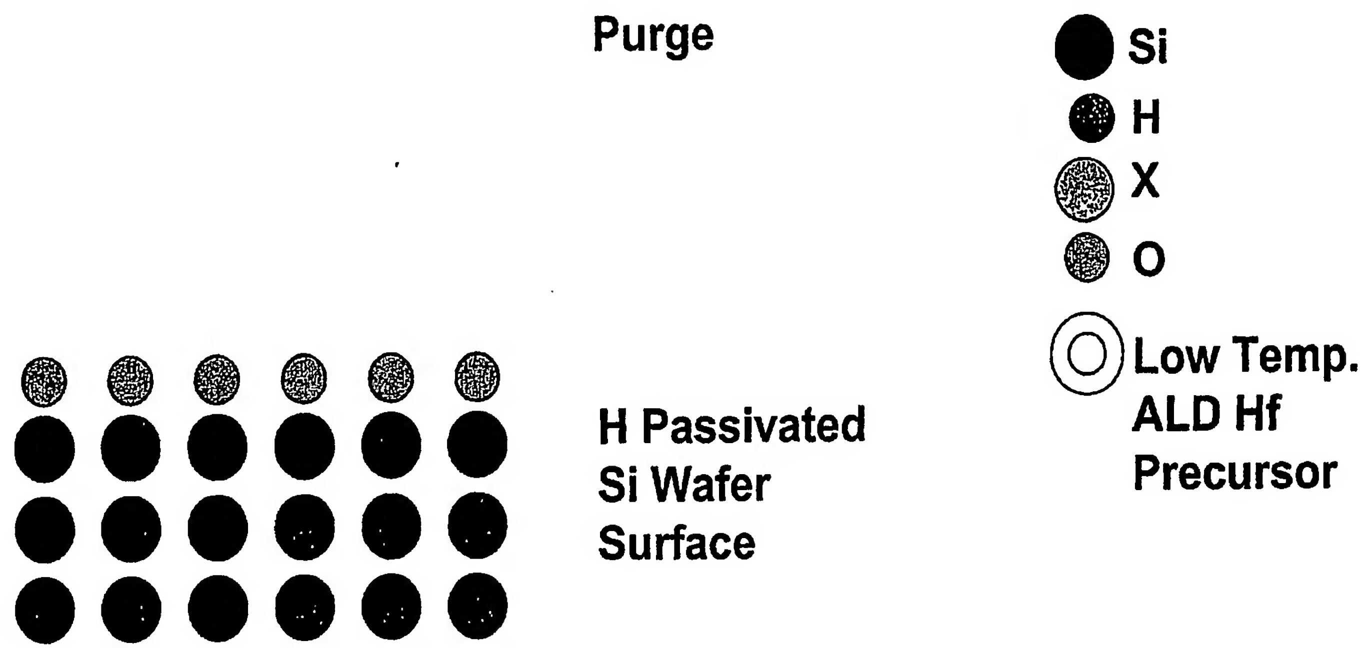
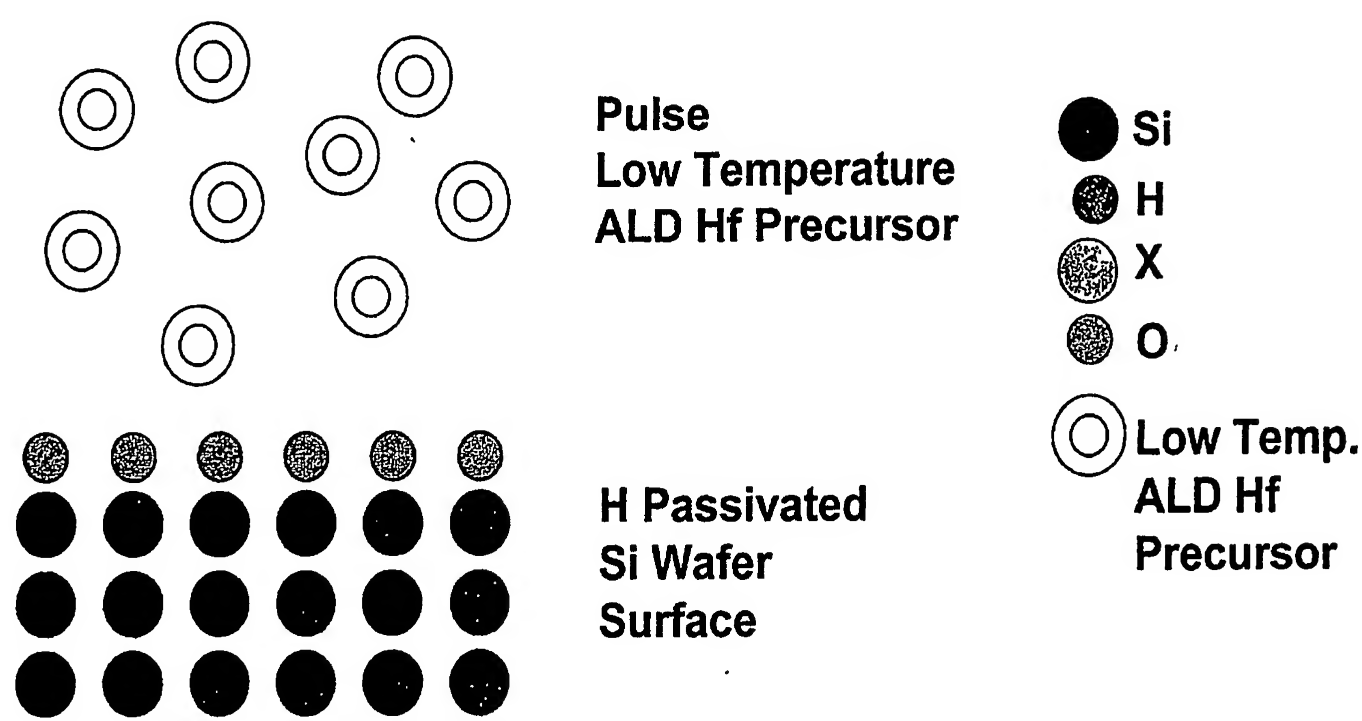


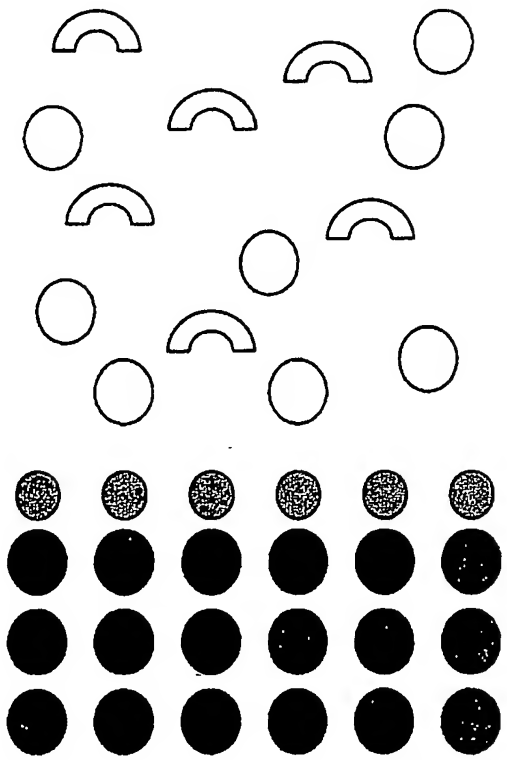
FIG - 4E

Atomic Layer Exchange For 5 EOT Gate Dielectric



FIG—4F

Atomic Layer Exchange For 5 EOT Gate Dielectric



Activate
Low Temp
ALD Hf Precursor

H Passivated
Si Wafer
Surface

Si
H
X
O

Low Temp.
ALD Hf
Precursor

FIG - 4G

Atomic Layer Exchange For 5 EOT Gate Dielectric

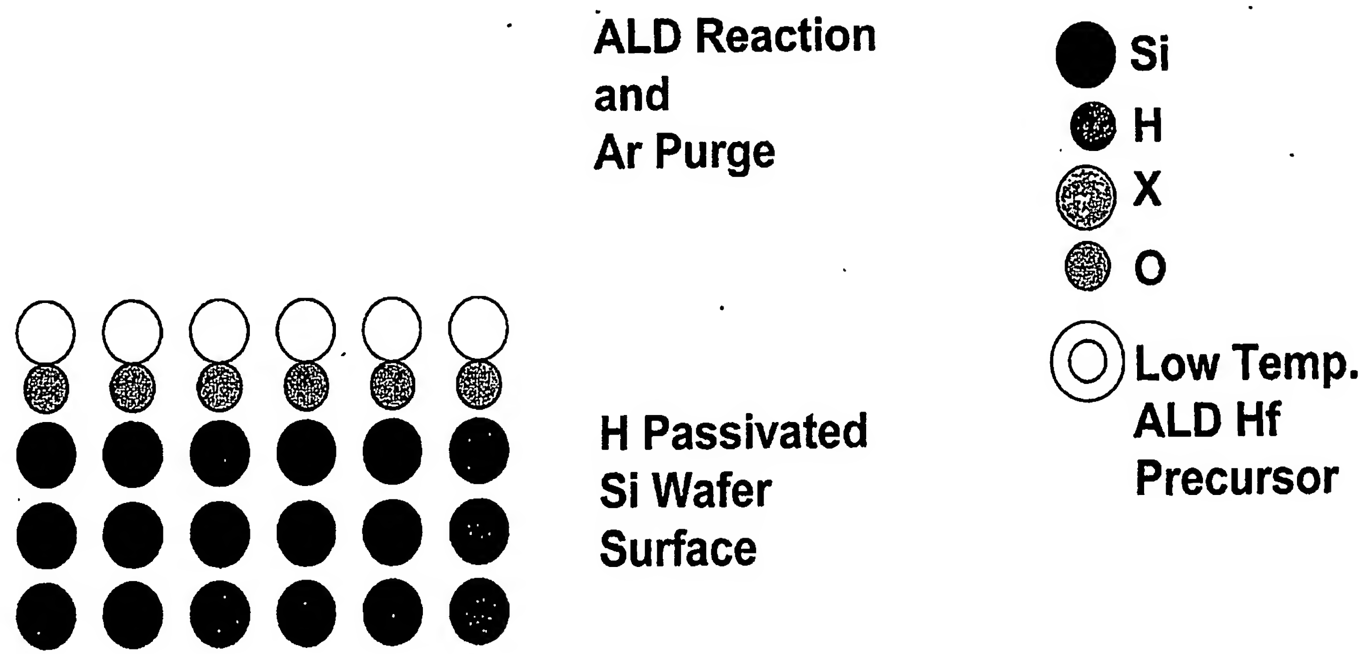
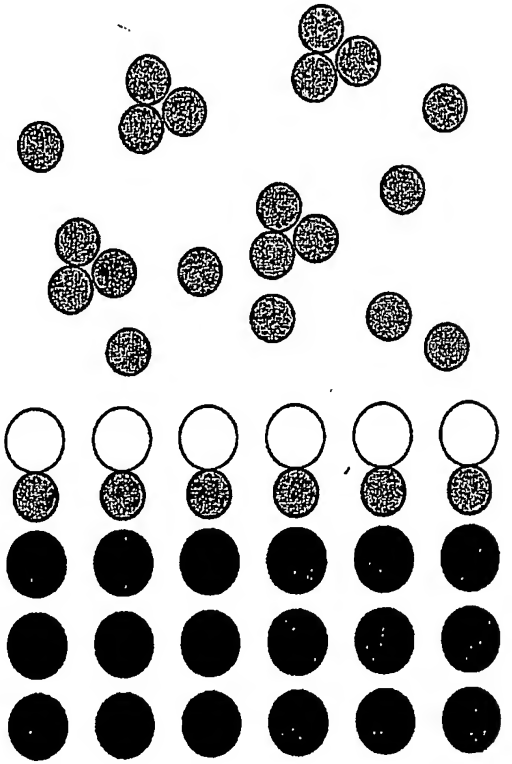


FIG – 4H

60391012.062302

Atomic Layer Exchange For 5 EOT Gate Dielectric



Pulse Oxygen Source and Activate

H Passivated Si Wafer Surface

Si
H
X
O

Low Temp. ALD Hf Precursor

FIG - 4I

Atomic Layer Exchange For 5 EOT Gate Dielectric

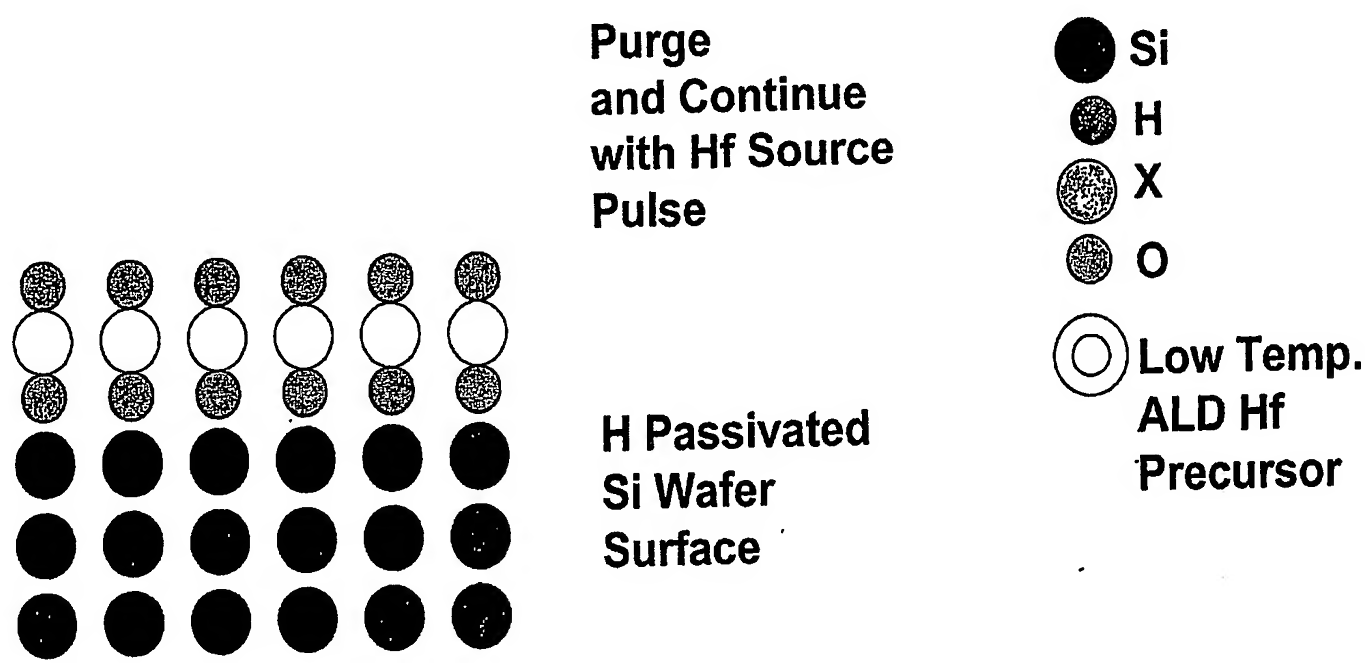


FIG_4J

New Liquid Hf Precursors for ALD Applications

	Formula	Appearance	b.p.(T_{sub})
TDMAH	$Hf[N(CH_3)_2]_4$	Light yellow crystal	85 /0.1mmHg
TEMAH	$Hf[C_2H_5N(CH_3)]_4$	Slightly yellow liquid	80 /0.1mmHg
TDEAH	$Hf[N(C_2H_5)_2]_4$	Light Yellow liquid	115 /0.1mmHg

FIG—5

New Liquid Zr Precursors for ALD Applications

	Formula	Appearance	b.p.(T_{sub})
TDMAZ	$Zr[N(CH_3)_2]_4$	Light yellow crystal	65 /0.1mmHg
TEMAZ	$Zr[C_2H_5N(CH_3)]_4$	Slightly yellow liquid	80 /0.1mmHg
TDEAZ	$Zr[N(C_2H_5)_2]_4$	Yellow liquid	112 /0.1mmHg

FIG—6

- Nano-laminates with multiple films and surfaces create more interface traps therefore not recommended for advanced gate applications.
- Bulk or Bi-Layer ALD Films are recommended.
- At Least One Atomic layer of SiO_2 is needed at the interface to control mobility.
- High-K Materials must be stable and do not react with H_2 treatment. High-K material oxides can react with H_2 and turn to metal films.
- Deposition process must take place at the lowest possible temperature in order to prevent diffusion of elements and minimize an interface depletion.
- ALD Precursors must be in liquid or gas form. Solid precursors are not recommended for volume production due to change in their partial pressure while they being are consumed.
- ALD Precursors should not decompose as in CVD reactions.
- Atomic, Layer by Layer growth is essential. Island type growth is not desired.
- Low temperature Deposition without any PLASMA assistance.

FIG – 7